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(54) Title: GLYCIDYL METHACRYLATE GRAFTED EPDM MODIFIERS IN FIBER REINFORCED POLYESTER COMPOSITIONS

(57) Abstract

Thermoplastic polyester, copolyester and polyblend molding compositions impact-modified by glycidyl methacrylate grafted EPDM exhibit high impact strength and good heat resistance when fibrous reinforcements, such as glass fibers are added to the blend.

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GLYCIDYL METHACRYLATE GRAFTED EPDM MODIFIERS
IN FIBER REINFORCED POLYESTER COMPOSITIONS

This invention relates to impact modified reinforced thermoplastic molding compositions and, more particularly, to glycidyl methacrylate or glycidyl acrylate grafted EPDM impact modifiers for fiber reinforced thermoplastic 5 polyester, copolyester and polyblend molding compositions.

BACKGROUND OF THE INVENTION

High molecular weight linear polyesters and copolymers of glycols and terephthalic or isophthalic acid have been available for a number of years. These are described 10 inter alia in Whinfield et al., U.S. 2,465,319, and in Pengilly, U.S. 3,047,539. These patents disclose that the polyesters are particularly advantageous as film and fiber formers.

With the development of molecular weight control, 15 the use of nucleating agents and two-step molding cycles, poly(ethylene terephthalate) or PET has become an important constituent of injection moldable compositions. Further, poly(1,4-butylene terephthalate) or PBT, because of its very rapid crystallization from the melt, is uniquely useful as a 20 component in such compositions. Work pieces molded from such polyester resins, in comparison with other thermoplastics, offer a high degree of surface hardness and abrasion resistance, high gloss and lower surface friction.

Furthermore, in particular, poly(1,4-butylene terephthalate) is much simpler to use in injection molding techniques than poly(ethylene terephthalate). For example, it is possible to injection mold poly(1,4-butylene terephthalate) 25 at low mold temperatures of from about 30° to 60°C. to produce highly crystalline, dimensionally stable moldings in short cycle times. Because of the high rate of crystallization, even at low temperatures, no difficulty is encountered 30 in removing the moldings from the molds. Additionally, the dimensional stability of poly(1,4-butylene terephthalate) in-

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jection moldings is very good even at temperatures near or well above the glass temperature of poly(1,4-butylene terephthalate).

However, the impact resistance of unmodified polyesters is relatively low at room temperature and below. Thus for many applications, it is desirable to have polyesters which are impact resistant at relatively high and relatively low ambient temperatures. Yet, the other mechanical properties such as modulus of elasticity, tensile strength at yield and at break should be impaired either not at all or only to an acceptable degree.

It has been recommended in various places to improve the impact resistance of polyesters by adding other polymers including interpolymers and copolymers. Specifically, the impact strength of thermoplastic linear crystalline polyesters, including poly(1,4-butylene terephthalate), has been improved by the incorporation therein of an ethylene-propylene nonconjugated diene rubbery terpolymer (EPDM). Although EPDM is capable of impact-modifying PBT polyester compositions, e.g., Coran et al., U.S. 4,141,863 and Tanaka et al., U.S. 4,290,927, such compositions often suffer from "incompatibility" resulting in streaks or delamination of molded or extruded parts.

In Hepp, European Patent Application 0 149 192, published July 24, 1985, there is disclosed a thermoplastic molding composition consisting of a thermoplastic resin, e.g., polyester, copolyester or block copolyester and an EPDM epoxidized with, e.g., m-chloroperoxy-benzoic acid. Although reinforcing agents, e.g., fibrous glass, may comprise up to about 50% by weight of such a composition, the examples given by this reference in Tables 1, 2 and 3 do not, however, exhibit a combination of good impact strength and acceptable knit-line characteristics.

Siegel, U.S. 3,769,260 discloses that a functionalized rubber improves impact strength of polyesters, and

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suggests a range of 0.02 to 20 microns in diameter for the dispersed rubber phase particles. Glass fibers are claimed as a filler in the '260 Patent but the unnotched Izod impact strengths are not particularly high.

5 Epstein, U.S. 4,172,859, discloses the use of random copolymers containing various polar monomers and glass fibers, up to 50 weight percent, are claimed as fibrous reinforcement. He also alludes to the use of materials grafted with various polar monomers, e.g., glycidyl methacrylate (GMA), to impact 10 modify thermoplastic polyesters including PBT and PET. However, this patent does not deal with and therefore fails to recognize one factor that is critical to the function of EPDM-g-GMA materials as impact modifiers for PBT systems. It does not recognize the benefits of reactive glycidyl 15 (meth)acrylates as graft monomers over non-reactive polar monomers such as maleic anhydride or n-vinyl pyrrolidone.

In the prior disclosures of Olivier, U.S. Patent Application, Serial No. 690,613, filed January 11, 1985, and Pratt et al., U. S. Patent Application Serial No. 004,089, 20 filed January 16, 1987, Attorney's Docket No. 337-1997 (8CT-4294), there are taught glycidyl methacrylate (GMA) grafted EPDM impact modifiers for polyester resins. In the specific examples, materials are described with high impact strengths. Best results are obtained with GMA contents of 25 above 2% by weight in the modifier. Moreover, no hint or suggestion is given in such prior disclosures that the impact modified compositions can or even should be reinforced, for example, with glass or other reinforcers.

It has now been surprisingly discovered that fibrous 30 reinforcing agents, such as glass fibers can be incorporated into thermoplastic polyester compositions comprising glycidyl methacrylate grafted EPDM (EPDM-g-GMA) impact modifiers, and that such compositions and glass fibers, will exhibit increased impact strength without significantly diminishing 35 the "stiffness" of the material as measured conveniently by

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tensile strength, and tensile and flexural modulus. For example, when PBT or PET is combined with EPDM-g-GMA, glass fibers, and, optionally, a nucleating agent, impact strength and resistance to heat are both enhanced.

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SUMMARY OF THE INVENTION

In accordance with the present invention are provided improved impact modified reinforced thermoplastic compositions comprising:

(a) a high molecular weight thermoplastic poly-
10 ester resin,

(b) an effective amount of an impact improving
rubbery polymer; and

(c) an effective amount of a fibrous reinforcing
agent wherein the improvement comprises using as said rubbery
15 polymer an EPDM terpolymer grafted with 2% or more by weight
based on said terpolymer of glycidyl methacrylate or glycidyl
acrylate or a mixture thereof, alone, or grafted in further
combination with a C₁-C₁₈ alkyl methacrylate or acrylate or a
mixture thereof.

20 Preferred features of the invention are compositions
as defined above wherein component (a) comprises poly(1,4-
butylene terephthalate) in an amount of from about 30 to about
80 parts by weight; component (b) comprises from about 1.5 to
about 35 parts by weight; and component (c) comprises glass
25 fibers in an amount of from about 5 to about 45 parts by
weight, based on a total composition of 100 parts by weight of
(a), (b) and (c) combined.

Also preferred are compositions as defined above
wherein component (a) comprises poly(ethylene terephthalate);
30 component (b) comprises a preblend of EPDM grafted with
glycidyl methyl methacrylate and poly(ethylene terephthalate)
in a ratio of from 1:1 to about 10:1 of the former to the
latter; component (c) comprises glass fibers; and further
comprising (d) an effective amount of a nucleating agent.

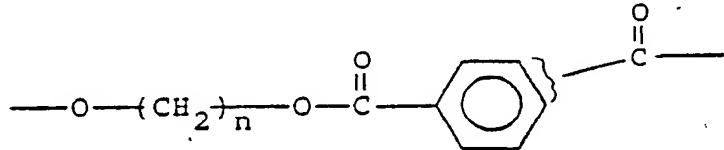
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DETAILED DESCRIPTION OF THE INVENTION

The high-molecular weight linear polyesters used as component (a) in the practice of the present invention are polymeric glycol esters of terephthalic acid and isophthalic acid. They are available commercially or can be prepared by known techniques, such as by the alcoholysis of esters of phthalic acid with a glycol and subsequent polymerization, by heating glycols with free acids or with halide derivatives thereof, and similar processes. These are described in U.S. 10 2,465,319 and U.S. 3,047,539, and elsewhere.

Although the glycol portion of the polyester can contain from 2 to 10 carbon atoms, it is preferred that it contain from 2 to 4 carbon atoms in the form of linear methylene chains.

15 Preferred polyesters will be of the family consisting of high molecular weight, polymeric glycol terephthalates or isophthalates having repeating units of the general formula:



wherein n is a whole number of from 2 to 4, and mixtures of 20 such esters, including copolymers of terephthalic and isophthalic acids of up to about 30 mole percent isophthalic units.

Especially preferred polyesters are poly(ethylene terephthalate) and poly(1,4-butylene terephthalate).

25 Illustratively, high molecular weight polyesters will have an intrinsic viscosity of at least about 0.7 deciliters/gram and, preferably, at least 0.8 deciliters/gram as measured in a 60:40 phenol-tetrachloroethane mixture at 30°C. At intrinsic viscosities of at least about 1.0 deciliters/ 30 gram, there is a further enhancement of toughness of the present compositions.

Copolyesters useful for the invention are preferably

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prepared from terephthalic acid and/or isophthalic acid and/or a reactive derivative thereof and one or more glycols, which may be a straight or branched chain aliphatic/cycloaliphatic glycol. Illustratively, the glycol will be ethylene glycol; 5 2-methyl-1,3-propanediol, 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 1,9-nonanediol; 1,10-decanediol; neopentyl-glycol; 1,4-cyclohexanediol; 1,4-cyclohexanediethanol; a mixture of any of the foregoing, or the like. Illustrative of suitable aliphatic dicarboxylic acids for the mixed 10 aromatic/aliphatic embodiments are suberic, sebacic, azelaic, and adipic acids and the like.

The copolyesters may be prepared by ester inter-change in accordance with the standard procedures. The co-polyesters may preferably be derived from at least 50% 15 butylene terephthalate units.

The block copolyesters useful in the composition of this invention are prepared by the reaction of terminally reactive poly(1,4-butylene terephthalate), preferably of low molecular weight, and a terminally reactive copolyester or 20 aliphatic polyester or both in the presence of a catalyst for transesterification, such as zinc acetate, manganese acetate, titanium esters, and the like. The terminal groups can comprise hydroxyl, carboxyl, carboalkoxy, and the like, including reactive derivatives thereof. After initial mixing, 25 polymerization is carried out under standard conditions, e.g., 220° to 280°C., in a high vacuum, e.g., 0.1 to 2 mm Hg, to form the block copolymer of minimum randomization in terms of distribution of chain segments. The result of reaction between two terminally reactive groups, of course, must be an 30 ester linkage. These copolyesters are described in a German Patent application P 27 56 167.7.

The copolyester designated component of these block copolyesters may be terminally reactive segments of copolyesters as described above. These copolyesters are most preferably derived from an aliphatic glycol and a mixture of 35

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aromatic and aliphatic dibasic acids in which the mole ratio concentration of aromatic to aliphatic acids is from between 1 to 9 to about 9 to 1, with an especially preferred range being from about 3 to 7 to about 7 to 3.

5 The terminally reactive aliphatic polyester component of these block copolyesters will contain substantially stoichiometric amounts of the aliphatic diol and the aliphatic dicarboxylic acid.

10 In addition to their ease of formation by well known procedures, both the aforementioned aromatic/aliphatic copolymers and aliphatic polyesters are commercially available. One source for such materials is the Ruco Division/Hooker Chemical Company, Hicksville, New York, which designates its compounds as "Rucoflex".

15 The block copolyesters used in the invention preferably comprise from about 95 to about 50 parts by weight based on the block copolyester of poly(1,4-butylene terephthalate) segments. The poly(1,4-butylene terephthalate) blocks, before incorporation into the block copolyesters, will preferably 20 have an intrinsic viscosity of about 0.1 dl./g. and, preferably, between about 0.1 and about 0.5 dl./g., as measured in a 60:40 mixture of phenol-tetrachloroethane at 30°C. The balance 50 to 5 parts by weight of the copolyester will comprise blocks of the aforementioned aromatic/aliphatic 25 copolyesters and/or aliphatic polyesters.

As will be understood by those skilled in the art, the poly(1,4-butylene terephthalate) block can be straight chain or branched, e.g., by use of a branching component, e.g., from about 0.05 to about 1 mole percent, based on terephthalate units of a branching component which contains at 30 least 3 ester-forming groups. This can be a polyol, e.g., pentaerythritol, trimethylol-propane, and the like or a polybasic acid compound, e.g., trimethyl trimestate, and the like.

Blends of the foregoing homopolymers, copolymers 35 and/or block copolymers or derivatives thereof are also use-

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ful for the invention.

The glycidyl ester grafted terpolymer additives used in the rubbery polymeric impact modifier (b) in this invention may be prepared from any of the well known EPDM terpolymer rubbers. EPDM terpolymers useful for preparing the grafted materials used in the invention are commercially available, e.g., Copolymer Corp. (EPSYN® 55), or may be prepared using a Ziegler-type catalyst. The preparation of typical EPDM terpolymers is described, for example, in 10 Gresham et al., U.S. 2,933,480; Tarney, U.S. 3,000,866; Guglielmino et al., U.S. 3,407,158; Gladding, U.S. 3,093,621 and U.S. 3,379,701. These terpolymers are characterized by the absence of chain or backbone unsaturation and the presence of sites of unsaturation in groups which are pendant to 15 or are in cyclic structures outside of the main polymer chain.

Useful EPDM terpolymers for the production of the glycidyl ether grafted terpolymers used in this invention comprise ethylene, a C₃ to C₁₆ straight or branched chain 20 alpha-olefin, preferably propylene, and a non-conjugated di-olefin. Satisfactory nonconjugated dienes that may be used as the third monomer in the terpolymer include straight chain dienes such as 1,4-hexanediene, cyclic dienes such as cyclo-octadiene and bridged cyclic dienes such as ethylidene 25 norbornene.

Preferred EPDM terpolymers are comprised of about 10-95, preferably 45-70 mole percent, by weight ethylene, about 5 to 90, preferably 30-55 mole percent polypropylene and a minor amount of diene monomer, most preferably a poly-30 unsaturated bridged ring hydrocarbon or halogenated derivative thereof, most preferably 5-ethylidene-2-norbornene. These EPDM terpolymers have a melt index of approximately 79 g/10 min., a Mooney viscosity of approximately 78 and a gram molecular weight of about 21,600.

35 The backbone rubber is subsequently graft modified

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with a graft monomer of epoxy functional acrylate or methacrylate. Although grafting may occur by various reaction mechanisms at practically any point on the backbone rubber, generally, the grafting takes place at an unreacted point of unsaturation on the polyene. For this reason, it is desirable to make use of an ethylene, mono-olefin, polyene backbone rubber having at least two unsaturated carbon-to-carbon linkages per 100 carbon atoms and little additional benefit is derived from the use of unsaturated backbone rubber having more than 20 carbon-to-carbon double bonds per 1000 carbon atoms. In the preferred practice of this invention, use is made of an unsaturated rubber having from 4-10 carbon-to-carbon double bonds per 1000 carbon atoms.

The point of ethylenic unsaturation on the epoxy functional graft monomer must be sufficiently reactive to react directly with the unsaturation of the polyene; or to react with a graft chain originating at, or for combination with, the polyene unsaturation. Such levels of reactivity require the alpha-beta situation of the ethylenic unsaturation as found in, for example, an epoxy functional esters of acrylic acid or alkyl acrylic acid. A free radical initiator, such as a dialkyl peroxide may be used to promote the graft reaction. Such initiator is generally used in an amount within the range of 1-5 parts per 100 parts by weight of the unsaturated rubber, and preferably in an amount within the range of 1-2 percent by weight.

Preferred as the graft monomer herein is glycidyl methacrylate (GMA).

The graft chain formed by the grafting process on the backbone rubber need not be a homopolymer or even be of entirely epoxy functional graft monomers. For example, combinations of the two above-mentioned epoxy functional graft monomers may be used as well as combinations of either or both with other C_1-C_{18} alkyl acrylates or methacrylates, wherein C_1-C_{18} may be straight chain or branched, e.g.,

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methyl, ethyl, isopropyl, 2-ethyl-hexyl, decyl, n-octodecyl, and the like. Particularly useful such comonomer grafts are grafts of glycidyl acrylate and/or glycidyl methacrylate and methyl methacrylate.

5 It is preferred in the present invention that the gel content of the elastomeric material be controlled either during polymerization or in subsequent processing to achieve a value of greater than about 10% by weight and less than 80%. With a gel content too low impact strength is high, but
10 knit line strength is low. With a gel content too high, the impact modifier is difficult to disperse.

Gel content in an especially convenient analysis, according to ASTM D-3616, is measured by the weight percent of remaining elastomeric material after extraction in hexane
15 or toluene. Gel content is an indication of the degree of cross-linking in the elastomeric material. Of course, persons skilled in the art are familiar with a variety of ways to control the degree of cross-linking and thus the gel content can be determined by numerous other methods. The cross-
20 link reaction may be a direct rubber backbone to rubber backbone joining, an epoxy functionality to epoxy functionality or rubber backbone joining, or a graft chain free radical addition to a second graft chain or to a rubber backbone. Further, cross-linking may be achieved by the addition of a
25 cross-linking agent to effectively achieve any of the above reactions. Thus, any of several steps to control gel content may be taken. Thermal aging will increase gel content. Increasing the amount of epoxy functional graft monomer will increase gel content. Increasing the amount of polyene mono-
30 ene monomer in the rubber backbone will increase gel content. The addition of a cross-linking agent will increase gel content. The use of graft monomers with greater tendency to cross-link will increase gel content, for example, a homopolymer graft of glycidyl acrylate will cross-link more
35 readily than a homopolymer graft of glycidyl methacrylate

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or a copolymer graft of glycidyl acrylate and methyl methacrylate.

As stated above, gel content of the elastomeric material used in this invention should range up to no higher than about 80%. Although cross-linking can be carried on well past this level, as has been mentioned, high levels of cross-linking diminish the dispersibility of the elastomeric material and lead to non-uniform mixing. Also, such high levels of localized cross-linking will create brittle areas within the elastomeric material which will decrease rubbery character. It is apparent that cross-linking should be uniformly dispersed throughout the elastomeric material.

It is preferred in the present invention that the elastomeric material have an epoxy functionality of at least 2.5 epoxy functionalities per 1000 carbon atoms, and preferably between about 5.0 and 13 epoxy functionalities per 1000 carbon atoms. Epoxy functionality means those epoxy sites which remain in the impact modifier resin after the loss of such functionalities as may react in the cross-linking reaction. In the instance of the use of GMA or GA as the epoxy functional graft monomer, a graft level of above about 1%, preferably above about 1.5% and most preferably above about 2% by weight is used to provide the minimum level of epoxy as shown above. The maximum is not particularly critical, e.g., up to 10-15% by weight can be used, but no special advantage is seen if these amounts are exceeded.

The grafting reaction may be carried out in solvent solution with the unsaturated rubber backbone present in a concentration which may range from 10-30 percent by weight, with constant stirring, at an elevated temperature within the range of 125-200°C. for a time ranging from 1/2 to 2 hours. The reaction condition can be varied depending somewhat upon the type and amount of catalyst and temperature conditions, as is well known to those skilled in the art. Where high amounts of graft monomer are to be attached to the backbone

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rubber, it has been found to be advantageous to carry out the graft reaction in the melt state of the backbone rubber, i.e., extruder grafting. This process is simply performed by feeding the backbone rubber, an excess of graft monomer, and 5 an appropriate catalyst to a melt extruder and mixing and reacting the feed components at an elevated temperature.

The fibrous reinforcing agents useful as component (c) in the practice of this invention comprise a range of materials including but not limited to glass, graphite, 10 wollastonite, carbons, metals, e.g., aluminum, iron, nickel, stainless steel and the like, titanates, e.g., titanate whiskers, quartz, mixtures of the foregoing and the like.

Although it is only necessary to have at least a reinforcing amount of the reinforcement present, in general, 15 the polyester component (a) will comprise from about 30 to about 80, preferably from about 40 to about 70, parts by weight, the rubbery polymer (b) will comprise from about 1.5 to 35, preferably 5 to 25 percent by weight, and the reinforcing agent (c) will comprise from about 1 to about 80 20 parts by weight of the total composition.

In particular, the preferred reinforcing fillers are of glass and it is preferred to use fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively soda free. This is known as "E" glass. However, 25 other glasses are useful where electrical properties are not so important, e.g., the low soda glass known as "C" glass. Special mention is made of glass filaments known as G- filaments. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical 30 pulling. The preferred filaments for plastics reinforcement are made by mechanical pulling. the filament diameters range from about 0.00012 to 0.00075 inch, but this is not critical to the present invention.

The length of the glass filaments and whether or 35 not they are bundled into fibers and the fibers bundled in

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turn to yarns, ropes or rovings, or woven into mats, and the like, are also not critical to the invention. However, in preparing the present compositions, it is convenient to use the filamentous glass in the form of chopped strands of from 5 about 1/8 inch to about 1 inch long, preferably less than 1/4 inch long. In articles molded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable, however, because the best properties are 10 exhibited by thermoplastic injection molded articles in which the filament lengths lie between about 0.000005 inch and 0.125 (1/8) inch.

In general, best properties will be obtained if the sized filamentous glass reinforcement comprises from about 1 15 to about 80% by weight based on the combined weight of glass and polyesters and preferably from about 5 to about 50% by weight. Especially preferably the glass will comprise from about 5 to about 40% by weight based on the combined weight of glass and resins. Generally, for direct molding use, up 20 to about 60% of glass can be present without causing flow problems. However, it is useful also to prepare the compositions containing substantially greater quantities, e.g., up to 70-80% by weight of glass. These concentrates can then be custom blended with blends of resins that are not glass reinforced to provide any desired glass content of a lower value. 25

The above described elastomeric material is physically dispersed in a thermoplastic polymer melt to form discrete particles of rubbery polymer in a continuous phase of a thermoplastic matrix resin or blend. At least an impact 30 strength improving amount of elastomeric material is dispersed in the matrix resin. Generally, this requires that the elastomeric material constitute at least 1.5 percent by weight, preferably 3.5 to 80 percent, most preferably 10 to 35 55 percent, by weight based on total thermoplastic content, including elastomeric material, of the molding composition.

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It will be apparent that, while the indicated composition range is optimum for making toughened rigid plastic articles, acceptable molding materials can still be made from mixtures with rubber contents much higher than this range. Thermo-
5 plastic elastomer type molding compounds are produced when the elastomer content exceeds 55 weight percent, and even mixtures above the phase inversion composition, i.e., those in which the thermoplastic resin phase is semi- or non- continuously interdispersed in a rubbery polymer matrix can
10 be used to make flexible molded articles with excellent properties. 80 weight percent elastomer is a typical upper limit. Compounding of the rubber, thermoplastic resin and reinforcing agent is carried out by standard techniques, for example, by simple melt blending or dry mixing and melt
15 extruding at an appropriate elevated temperature for any given thermoplastic matrix. The resultant admixture is then molded into a thermoplastic piece of specific dimensions or further extruded into a film or sheet product.

It is important to the final properties of molded
20 parts containing elastomeric material that there is sufficient mixing in the extrusion of the resin melt. Herein, several reactions have been taught or suggested to take place in the extruder and such are, of course, effected by mixing as well as residence time in the extruder. Thus, thorough
25 mixing of the polymer melt is suggested and, depending upon the equipment employed, two successive extrusions of the melt may be required.

As has been mentioned, in preferred compositions the particle size of the rubber grafted with glycidyl esters will
30 be selected to provide that at least 60 weight percent of such particles, and preferably more than 70 weight percent of them are greater than 1 micron in diameter. Such compositions combine optimum notched Izod impact strength, with knit-line strength, and these are vastly superior to those obtained
35 with compositions wherein, for example, only about 50 weight

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percent of the particles exceed 1 micron in diameter. Particle size can be measured in any of the ways known in this art, but an especially convenient way is to use a computerized particle size analyzer to measure photomicrographs of 5 scanning electron microscopy (SEM) images.

Compounding can be carried out in conventional equipment. For example, after pre-drying the thermoplastic polyester resin, e.g., at 125°C. for 4 hours, a single screw extruder is fed with a dry blend of the polyester, reinforcing agent and the additive ingredients, the screw employed 10 having a long transition and metering section to insure melting. On the other hand, a twin screw extrusion machine, e.g., a 28 mm Werner Pfleiderer machine can be fed with resin and additives at the feed port. In either case, a generally 15 suitable machine temperature will be about 450°F. to 520°F.

The compounded composition can be extruded and cut up into molding components such as conventional granules, pellets, etc., by standard techniques.

The compositions of this invention can be molded in 20 any equipment conventionally used for thermoplastic compositions. For example, with poly(1,4-butylene terephthalate) good results will be obtained in an injection molding machine, e.g., of the Newbury type with conventional cylinder temperature, e.g., 480-500°F. and conventional mold temperatures, 25 e.g., 150°F. On the other hand, with poly(ethylene terephthalate), because of the lack of uniformity of crystallization from interior to exterior of thick pieces, somewhat less conventional but still well known techniques can be used. For example, a nucleating agent such as a LiOH, sodium 30 stearate, graphite or a metal oxide, e.g., ZnO or MgO can be included as component (d) and standard mold temperatures of from about 150°F. to 230°F. will be used.

It is to be understood that the foregoing compositions may contain other additives known in the art, including, but without limitation, nucleating agents, mold release 35

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agents, flow promoters, coloring agents, coupling agents, and stabilizers. The elastomeric containing molding compositions of this invention may be used as molding pellets and may contain pigments, dyes, stabilizers, plasticizers, and the 5 like. One may readily determine which are necessary and suitable for a particular application.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the preferred invention. The claims are not to be construed to be limited by 10 them in any manner whatsoever.

EXAMPLE 1

An impact modified glass reinforced PBT composition was prepared and suitable workpieces were molded for testing. EPDM grafted with 4.5% glycidyl methacrylate (EPDM-g-GMA) and 15 a 21% gel content was used as an impact modifier. The modifier can be prepared by use of a procedure in copending application 337-1997 (8CT-4294), e.g., Example 9(a). Typically, 100 parts by weight of backbone rubber, EPSYN®55 resin, EPDM rubber (23 RSV 9C=C/1000 C; 8% by weight of polyene 20 5-ethylidene-2-norbornene; ethylene/propylene ratio = 2.1; Mooney Viscosity = 50; (Copolymer Chemical and Rubber Corporation); 0.1 parts by weight of hindered phenolic antioxidant, IRGANOX®1076, Ciba-Geigy Corporation; 7.4 parts by weight of glycidyl methacrylate; and 0.56 parts by weight of 2,5-di- 25 methyl-2,5-di(t-butyl-peroxy) hexane initiator can be passed through a Werner-Pfleiderer WP57 twin screw extruder. Zone temperatures of 200°C. and screw speeds of 150 rpm can be used. The water cooled strands of elastomeric material which emerge can be chopped into pellets. The blend with PBT was 30 the tumble-mixed and extruded one time through a Prodex 2½" extruder equipped with a double wave screw. The material was subsequently dried and molded on a 75 ton Cincinnati injection molding machine. The composition and results are set forth in Table 1:

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TABLE 1: Glass Reinforced Thermoplastic
Composition PBT/EPDM-g-GMA Terpolymers

<u>Example</u>	<u>1</u>
<u>Composition (parts by weight)</u>	
5 PBT	55
EPDM-g-GMA	15
Glass fiber, 1/8" chopped strands	30
<u>Properties</u>	
Notched Izod. (ft.lb./in.)	4.1
10 Flexural Modulus (psi)	750,000
Tensile Strength (psi)	14,200
Tensile Modulus (psi)	809,000

The results above indicate that the EPDM-g-GMA modified PBT composition exhibits excellent mechanical properties, e.g., flexural modulus, tensile strength and tensile modulus and impact strength.

The molded article prepared in Example 1 was examined under a scanning electron microscope (SEM). In the EPDM-g-GMA impact modified glass reinforced composition, the fibers showed no separation from the matrix and the exposed fibers had very rough surfaces, indicating a high degree of adhesion of the matrix to the glass.

EXAMPLE 2-5

Glass reinforced impact modified PET compositions were prepared in accordance with this invention. As the impact modifier, a preblended combination of 25% PET and 75% EPDM-g-GMA was added. Compositions and test results are set forth in Table 2.

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TABLE 2: Thermoplastic Compositions PET/EPDM-g-GMA/Glass

<u>Example</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
<u>Composition (parts by weight)</u>				
PET ^a	60.35	52.35	58.35	50.35
PET/EPDM-g-GMA Conc. ^b	8.0	16.0	8.0	16.0
G-Filament Glass ^c	30.0	30.0	30.0	30.0
Nucleating agent ^d	--	--	0.3	0.3
Additives for stabilization	1.65	1.65	1.65	1.65
<u>Results</u>				
Heat Distortion, °F. 264 psi	272	390	440	430
Notched Izod, ft.lbs./in.	2.0	2.9	1.9	2.3
Unnotched Izod, ft.lbs./in.	13.7	14.7	14.0	14.5
Flexural Strength, psi	24,600	22,500	29,000	25,800
Flexural Modulus, 10 ⁶ psi	1.00	0.90	1.19	0.96
Tensile Strength, psi	13,500	14,000	18,100	15,600
Specific gravity	1.500	1.456	1.534	1.469
Melt viscosity, pellets, 510°F.	9,000	41,700	18,600	88,100
Notched Izod, -30°C.	1.8	2.3	1.9	2.1
Tensile elongation, %	7.4	10.4	8.2	8.9
Flexural elongation, %	4.1	4.3	3.4	3.8

a X5202A, Rohm & Haas Company

b 75% EPDM-g-GMA/25% PET

c 1/8" chopped strand

d sodium stearate

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The above results indicate that articles of high impact strength can be produced by the addition of EPDM-g-GMA to 30% glass reinforced nucleated PET compositions.

EXAMPLES 6-15

5 In the following Examples 6-15, the EPDM-g-GMA and glass contents were varied. PBT compositions were blended according to the procedure of Example 1 except that a Buss Kneader was used for extrusion. Articles suitable for testing were molded. Compositions and test results are set forth in
10 Table 3.

TABLE 3: Thermoplastic Compositions PBT/EPDM-g-GMA/Glass

Example	6A	6	7	8	9	10	11	12	13	14	15
<u>Composition (parts by weight)</u>											
PBT ^a	100	77	67	52	80	70	55	84	59	67	52
PBT/EPDM-g-GMA ^b	--	18	18	18	15	15	15	11	11	18	18
Glass ^c	--	5	15	30	5	15	30	5	30	15	30
<u>Results</u>											
Notched Izod, ft.lbs./in.	1.0	6.3	5.4	5.7	5.2	4.9	5.2	3.9	3.8	4.1	5.9
Unnotched Izod, ft.lbs./in.											
Double Gate	2.6	10	9	10	10	12	11	12	6	6	9
Flexural Modulus, psi x 10 ⁵	9.67	2.15	3.49	4.92	2.50	4.00	6.33	2.89	7.30	3.81	6.10
Flexural Elongation to Break, in.	0.33	0.81	0.46	0.37	0.63	0.40	0.31	0.65	0.30	0.33	0.30
Tensile Modulus, psi x 10 ⁵	8.08	3.29	4.69	6.59	3.58	4.77	7.71	3.41	7.95	4.50	8.08
Tensile Elongation, %	4.6	12.4	8.5	3.6	9.3	4.0	3.3	10.4	5.4	6.4	5.7
Heat Distortion Temperature, °C., 264 psi	207	58	64	184	64	173	196	71	191	177	182

^a Valox®315, General Electric Company^b added as a 25 PBT-75 EPDM-g-GMA concentrate^c 1/8" chopped strands

1 Valox®295, General Electric Company

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The results indicate that compositions of high impact strength and good resistance to heat can be prepared in accordance with the present invention.

EXAMPLES 16-18

5 Impact-modified glass reinforced compositions of PBT and PBT/PET were blended following the procedure set forth in Example 1. Workpieces suitable for testing were prepared. The compositions used and the data obtained are given in Table 4.

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TABLE 4: Thermoplastic Compositions PBT/EPDM-g-GMA/Glass

<u>Example</u>	<u>16A</u>	<u>16B</u>	<u>16</u>	<u>17</u>	<u>18</u>
<u>Composition (parts by weight)</u>					
PBT	79.85 ¹	73.15 ¹	69.85 ¹	49.85 ²	29.75 ²
PET	--	--	--	--	20.0
PBT/EPDM Conc. ^a	20.0	26.7	20.0	20.0	20.0
Glass ^b	--	--	10.0	30.0	30.0
<u>Additives for stability</u>					
and mold release	0.15	0.15	0.15	0.15	0.25
<u>Results</u>					
Heat Distortion, °F, 264 psi	205	207	252	378	360
Notched Izod, ft.lbs./in.	16.1	21.0	3.5	4.7	4.8
Unnotched Izod, ft.lbs./in.	NB	NB	20.2		17.57
Flexural Strength, psi	8,800	800	10,400	17,000	17,200
Flexural Modulus, kpsi	251.2	221.1	336.6	733.6	753
Tensile Strength, psi	6,300	5,900	7,600	11,500	11,600
Specific Gravity	1.217	1.2016	1.275	1.412	1.425
Tensile Elongation	228	189	15	10	11
<u>Flexural Elongation</u>	--	--	18.9	5.31	4.99

1 Valox®315, General Electric Company

2 Valox®295, General Electric Company

a See footnote, Table 3

b 1/8 inch chopped strand

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The data above indicate that reinforced impact modified polyester compositions are prepared in accordance with this invention.

The above patents, applications and publications
5 are incorporated herein by reference.

Many variations will suggest themselves to those skilled in the art in light of the above, detailed description. For example, instead of using poly(1,4-butylene terephthalate) or poly(ethylene terephthalate) as component (a),
10 other polyester resins, such as copolyesters derived from one or more aliphatic and/or aromatic dicarboxylic acids and one or more straight or branched chain aliphatic or cycloaliphatic glycols including random or block copolyesters. Instead of injection molding, blow molding, including injection blow
15 molding can be used. Instead of glycidyl methacrylate, a mixture of glycidyl methacrylate and methyl methacrylate, a mixture of glycidyl acrylate and methyl methacrylate or a mixture of glycidyl methacrylate and octadecyl methacrylate or glycidyl acrylate alone can be used. Furthermore, other
20 additives known to those skilled in the art may be added in conventional amounts to the impact modified compositions herein including but without limitation, nucleating agents, mold release agents, flow promoters, coloring agents, flame retardants, coupling agents and stabilizers.

25 All such obvious variations are within the full intended scope of the appended claims.

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CLAIMS:

1. An improved impact modified reinforced thermoplastic composition comprising:
 - (a) a high molecular weight thermoplastic polyester resin,
 - 5 (b) an effective amount of an impact improving amount of a rubbery polymer; and
 - (c) an effective amount of a fibrous reinforcing agent wherein the improvement comprises using as said rubbery polymer an EPDM terpolymer grafted with 2% or more by weight
 - 10 based on said terpolymer of glycidyl methacrylate or glycidyl acrylate or a mixture thereof.
2. A composition of Claim 1 wherein said fibrous reinforcing agent (c) is selected from the group consisting of glass, metals, ceramics, silicates, quartz, and carbons.
3. A composition as defined in Claim 1 wherein said fibrous reinforcing agent (c) is glass.
4. A composition as defined in Claim 1 wherein the grafted EPDM terpolymer is derived from approximately 45 to 70 mole percent ethylene, approximately 30 to 55 mole percent propylene and a minor amount of 5-ethylidene-2-norbornene.
5. A composition of Claim 1 wherein the EPDM-glycidyl ester grafted terpolymer is present in an amount of, approximately, 1.5 to 35 percent by weight based on the total composition.
6. A composition of Claim 1 wherein the grafted EPDM terpolymer is present in an amount of, approximately, 5 to 25 percent by weight based on the total composition, (a), (b) and (c).
7. A composition as defined in Claim 1 wherein the high-molecular weight thermoplastic polyester resin (a) is selected from the group comprising poly(ethylene terephthalate), poly(1,4-butylene terephthalate), copolyesters, or any 5 combination thereof.

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8. A composition of Claim 7 wherein the thermoplastic polyester resin (a) is poly(1,4-butylene terephthalate).

9. A composition of Claim 7 wherein the thermoplastic polyester resin (a) is poly(ethylene terephthalate).

10. A composition of Claim 7 wherein the thermoplastic polyester resin (a) is a copolyester derived from one or more aliphatic and/or aromatic dicarboxylic acids and one or more straight or branched chain aliphatic or cycloaliphatic glycols.

11. A composition of Claim 10 wherein the copolyester is a random copolyester.

12. A composition of Claim 10 wherein the copolyester is a block copolyester.

13. A composition of Claim 7 wherein the thermoplastic polyester resin (a) is a polyblend of poly(ethylene terephthalate) and poly(1,4-butylene terephthalate).

14. A composition as defined in Claim 1 wherein component (a) comprises poly(1,4-butylene terephthalate) in an amount of from about 30 to about 80 parts by weight; component (b) comprises from about 1.5 to about 35 parts by weight; and component (c) comprises glass fibers in an amount of from about 5 to about 45 parts by weight, based on a total composition of 100 parts by weight of (a), (b) and (c) combined.

15. A composition as defined in Claim 1 wherein component (a) comprises poly(ethylene terephthalate); component (b) comprises a preblend of EPDM grafted with glycidyl methacrylate and poly(ethylene terephthalate) in a ratio of from 1:1 to about 10:1 of the former to the latter; component (c) comprises glass fibers; and further comprising (d) an effective amount of a nucleating agent.

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16. A composition as defined in Claim 15 wherein component (a) comprises an amount of from about 30 to about 80 parts by weight; component (b) comprises an amount of from about 1.5 to about 35 parts by weight; component (c) 5 comprises an amount of from about 5 to about 45 parts by weight, and component (d) comprises an amount of from about 0.5 to about 5 parts by weight, based on a total weight of 100 parts of (a), (b), (c) and (d) combined.

17. In a process for producing a reinforced impact modified thermoplastic molding composition comprising blending

(a) a high molecular weight thermoplastic 5 polyester resin;

(b) an effective amount of an impact improving amount of a rubbery polymer; and

(c) an effective amount of a fibrous reinforcing agent, the improvement which comprises using as said 10 rubbery polymer an EPDM terpolymer grafted with 2% or more by weight based on said terpolymer of glycidyl methacrylate or glycidyl acrylate or a mixture thereof, alone, or grafted in further combination with a C₁-C₁₈ alkyl methacrylate or acrylate or a mixture thereof, said impact modifier having a 15 gel content in the range of from about 10 to about 80% by weight.

18. A process as defined in Claim 17 wherein said fibrous reinforcing agent (c) is selected from the group consisting of glass, metals, ceramics, silicates, quartz and carbons.

19. A process as defined in Claim 17 wherein the high molecular weight thermoplastic polyester resin (a) is selected from the group comprising poly(ethylene terephthalate), poly(1,4-butylene terephthalate), a copolyester, or any 5 combination thereof.

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20. A process as defined in Claim 17 wherein the high molecular weight thermoplastic polyester is poly(1,4-butylene terephthalate).

21. A process as defined in Claim 20 wherein the high molecular weight thermoplastic polyester is poly(ethylene terephthalate).

22. A process as defined in Claim 17 wherein the reinforcing agent comprises glass fibers.

23. An article of manufacture thermoformed from an impact modified thermoplastic composition as defined in Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 88/00676

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁴

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC ⁴ : C 08 L 67/02; C 08 K 7/02; // (C 08 L 67/02, 51/06)

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC ⁴	C 08 L

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	WO, A, 86/04076 (COPOLYMER RUBBER AND CHEMICAL CORP.) 17 July 1986, see claims 1-36 cited in the application --	1-23
Y	FR, A, 2311808 (E.J. DU PONT DE NEMOURS AND CO.) 17 December 1976, see claims 1, 9,10; page 12, lines 13-14 cited in the application -----	1-23

* Special categories of cited documents: ¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

3rd August 1988

Date of Mailing of this International Search Report

26 AUG 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

P.C.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 8800676
SA 22804

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 18/08/88.
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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